



SAFETY IN STORAGE, HANDLING AND DISTRIBUTION OF LIQUID HYDROGEN

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Prepared by WG-6 Cryogenic vessels

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Amendments from 06/02

Section	Change
	<u>Editorial to align style with EIGA Style Manual</u>
3	<u>New section on definitions</u>
4.5	<u>Section expanded to cover steel properties</u>
5.1.2	<u>Removal of Table 2</u>
5.1.7	<u>Vent stack design details added</u>
5.5.2.4	<u>Vaporiser inspection requirements added</u>
8	<u>New reference section added</u>
Appendix A	<u>Appendix A removed as redundant</u>

Note: Technical changes from the previous edition are underlined

1 Introduction

Because of the growth in the availability and use of liquid hydrogen in Europe, the European Industrial Gases Association (EIGA) has recognised the need for a publication addressing safety in storage, handling and distribution of liquid hydrogen.

This EIGA publication is intended as guidance for companies directly associated with the installation of liquid hydrogen storage at the user's premises and the distribution of liquid hydrogen by road, rail and sea transport.

Because of the properties of liquid hydrogen, specific precautions shall be taken and these are described in this publication.

2 Scope and purpose

2.1 Scope

A liquid hydrogen storage installation on a user's premises is defined for the purpose of this publication as the installed liquid storage tank. This publication applies to the layout, design and operation of fixed storages and the transportation of liquid hydrogen in bulk form by tankers or tank containers, by road, sea and rail, to fixed storages at user's premises. Portable containers, such as pallet tanks and liquid cylinders, are excluded from the scope of this publication.

2.2 Purpose

To provide recommendations on the storage, handling and distribution of liquid hydrogen.

3 Definitions

For the purpose of this publication the following definitions apply.

3.1 Publications terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May and need not

Indicates that the procedure is optional.

3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

4 Properties and effects of hydrogen

4.1 General

Liquid hydrogen has the UN number 1966.

Liquid hydrogen is accompanied by a certain amount of gaseous hydrogen. For this reason, it is necessary to consider properties of both liquid and gaseous hydrogen. Some common properties of hydrogen are summarised in Table 1.

4.2 Physical properties

Hydrogen is the least dense of all gases. At standard temperature and pressure, the density of gaseous hydrogen is one fourteenth that of air. Due to its low density, gaseous hydrogen will rise and diffuse rapidly in the air. Hydrogen can therefore collect in the roof spaces of buildings. Hydrogen can diffuse rapidly through certain porous materials or systems with small openings that would normally be gastight compared to air.

At ambient temperature, gaseous hydrogen, contrarily to most other gases, is heated by throttled expansion. The temperature rise is only small and this alone cannot cause self-ignition.

The thermal conductivity of hydrogen is typically higher than that of other gases. This influences combustion behaviour, for example burning velocity.

4.3 Chemical properties

Hydrogen is not significantly reactive. Hydrogen is not corrosive but depending on temperature, pressure and other conditions it can cause embrittlement of certain steels.

From the chemical point of view, hydrogen is a reducing agent. Hydrogen is flammable and therefore presents a possible explosion hazard.

Hydrogen is easily ignited; its minimum ignition energy is very low (19μJ). In practice hydrogen venting or leaking to atmosphere, particularly from a pressure source can ignite due to electrostatic or self-igniting impurities in the hydrogen.

Hydrogen burns with a hot flame. Burning hydrogen produces no soot. Therefore, the flame is pale, colourless and almost invisible in daylight. The heat radiated by a hydrogen flame is relatively low (only 10 percent that of propane). Therefore, a hydrogen flame gives little warning of its presence either by sight or heat.

The range of flammability both in air and oxygen is wide (4-75%). Confined mixtures of hydrogen and air or oxygen explode very strongly and can detonate (typical explosivity range in air is 16-56%). An unconfined gas cloud explosion of hydrogen is very unlikely to occur and to date such a detonation has not been observed.

Hydrogen flames, especially those emanating from a high-pressure source, are extremely difficult to extinguish. The preferred method of extinguishing a hydrogen flame is to shut off the flow.

4.4 Biological effects

Hydrogen is colourless (transparent), odourless and tasteless and therefore not detectable by the human senses. Hydrogen is not toxic but can act as an asphyxiant by displacing the oxygen in the surrounding air.

Breathing a pure hydrogen atmosphere will produce immediate loss of consciousness and almost immediate death. The amount of hydrogen necessary to produce dangerous oxygen deficiency is significantly higher than the lower flammability limit. Therefore, the primary risk of hydrogen is not asphyxiation but fire and explosion.

Liquid hydrogen has specific effects on the human body (see below).

4.5 Properties and effects of liquid hydrogen

Liquid hydrogen is colourless and odourless. Its density is one fourteenth that of water. Liquid hydrogen is extremely cold -and except for helium- has the lowest boiling point of all gases.

Hydrogen consists of ortho-hydrogen and para-hydrogen. These forms have differences in physical but not in chemical properties. At the temperature of liquid hydrogen ortho-hydrogen tends to convert into para-hydrogen. This conversion liberates heat that encourages evaporation. However, commercial liquid hydrogen mainly consists of para-hydrogen.

Liquid hydrogen and the cold "boil off" gas, evolving from the liquid, can produce severe burns (similar to thermal burns) upon contact with skin. Delicate tissue, such as those of the eyes can be injured by exposure to the cold gas or splashed liquid in a brief period of time, that would normally be too short to affect the skin of the hands or face. Contact between unprotected parts of the body with uninsulated piping or vessels containing liquid hydrogen can cause the flesh to stick and tear.

Liquid hydrogen and cold "boil off" gas can cause many common materials such as carbon steel, plastic or rubber to become brittle and prone to fracture under stress.

At the temperature of liquid hydrogen all gases, except helium, condense and then solidify. Such solid particles can plug restricted areas such as valves and orifices, which could lead to a failure of, flow and/or pressure increase. Furthermore, condensed or solidified air in liquid hydrogen is a potential explosion hazard.

Liquid hydrogen has a very low heat of vaporisation (related to a volume basis). Therefore, a small heat input for example inserting solids or liquids at room temperature will create a violent evolution of gas and splashing of liquid.

Liquid hydrogen in poorly insulated or uninsulated containers and piping will liquefy the surrounding air. Due to the different boiling points of nitrogen and oxygen condensed air is oxygen-enriched and can cause a fire risk.

Liquid hydrogen, spilled to the atmosphere evaporates rapidly. One litre of liquid hydrogen gives approximately 850 litres of gaseous hydrogen at ambient conditions.

Cold boil-off hydrogen is a little denser than air and may accumulate in pits and trenches, for short periods depending on temperature and quantity. After that hydrogen rises and diffuses rapidly.

Cold boil-off hydrogen condenses the moisture in the air, thus creating a highly visible fog.

4.5.1 Implications for inner vessel design and manufacture

Typically, the inner vessel is manufactured with 300 series austenitic stainless steels. Type 304 SS has shown a tendency to experience hydrogen embrittlement in highly stressed parts like cold formed heads. Pressure vessel heads made of 304 SS should be solution annealed after cold forming in order to reduce the residual stresses.

Note: Annealing could be difficult on large heads.

Care should be taken during fabrication not to leave tool marks or other stress risers on the inner surface of the pressure vessel, which can be propagation sites for hydrogen embrittlement.

It is also recommended to limit the ferrite in the welds

Table 1 Properties of hydrogen and some comparable substances

(Values taken from a number of sources)

	Valid at		Hydrogen ¹	Methane	Propane	Heptane ³
Boiling point	1.013 bara	K	20.4	111.6	231.1	371.5
Critical temperature		K	33.19	119.6	396.8	540.4
Critical pressure		bara	13.15	46.0	42.4	27.5
Density of liquid	Boiling point	kg/m ³	70.8	422.5	580.7	680.4
Heat of vaporisation	Boiling point	kJ/kg	445.6	510.4	427.8	317.0
Density of gas	Boiling point	kg/m ³	1.338	1.818	2.419	3.29
Density of gas	1.013 bara 0°C	kg/m ³	0.090	0.717	2.011	4.46
Specific heat, C _p	1.013 bara 0°C	kJ/kg K	14.19	2.19	1.56	1.70 ⁵
Specific heat, C _v	1.013 bara 0°C	kJ/kg K	10.06	1.67	1.35	N/A
Thermal conductivity	1.013 bara 0°C	W/m K	0.1682	0.0305	N/A	0.0188 ⁶
Diffusion coefficient (in air)	1.013 bara 20°C	cm ² /S	0.69	0.22	0.12	0.05
Limits of flammability ²	1.013 bara 20°C	Vol.-%	4.0-75.0	5.0-15.4	2.1-9.5	1.11-6.7
Auto ignition temperature ²	1.013 bara	°C	560	595	470	215
Minimum ignition energy ²	1.013 bara 20°C	mJ	0.019	0.28	0.26	0.22
Theoretical temperature of flame ²	1.013 bara	°C	2045	1875	2040	2200

1. Normal hydrogen (75% ortho and 25% para)
2. Combustion with air
3. As a representative for gasoline
4. At 0°C
5. Vapour at 25 °C
6. Vapour at 100°C

Conversion: 1bar = 10⁵ Pa